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The Influence of The Weight of N,N'-Methylene-Bis-Acrylamide as Crosslinker on The Ability of Chitosan-Graft-Poly (Acrylic Acid) Superabsorbent to Water Retention in Sandy Soil

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Abstract

Enhancing the agricultural productivity of sandy soil can be achieved by incorporating a superabsorbent material that serves dual purposes: improving water retention and gradually releasing fertilizer nutrients. The objective of this study is to determine the influence of the weight of N,N'-methylene-bis-acrylamide (MBA) as a crosslinker in chitosan-graft-poly(acrylic acid) superabsorbent on water holding and water retention in sandy soil. The superabsorbent was prepared by mixing a chitosan solution with ammonium persulfate as a catalyst and acrylic acid, which had been neutralized with KOH. Subsequently, the mixture was cross-linked using MBA. The resulting superabsorbent indicated that an increase in the weight of MBA decreased the swelling ratio and increased water retention due to a denser network structure. The water holding capacity for superabsorbent prepared with all MBA weights was nearly the same. The highest swelling ratio and water retention were 167.552 g/g and contained 7.6% water on day 7 for the superabsorbent crosslinked with 0.015 g of MBA.

INTRODUCTION

Sandy soil has high water permeability, low water-holding capacity, and low nutrient retention and exchange capability. Sandy soil has weak soil structure and is susceptible to wind erosion (Yost & Hartemink, 2019). Due to the limited availability of agricultural land caused by the conversion of land for industry and housing, the development of sandy soil for agriculture is necessary. Given that sandy soil does not meet the requirements for agriculture, such as nutrient content and water-holding capacity, it is necessary to add superabsorbents to improve these two functions. Agriculture heavily relies on water, making up 70% of the world's water usage. Around 24% of the Earth's total land area is affected by desertification worldwide. Effective management of water resources is crucial for combating desertification. Hence, there's an urgent need to use water more efficiently in agriculture to address water scarcity and enhance soil quality (Niu et al., 2024).

Improving the productivity of sandy soil for agriculture can be achieved by incorporating a superabsorbent material that serves dual purposes: enhancing water retention and gradually releasing fertilizer nutrients (Jayanudin et al., 2022; Niu et al., 2024). Commercial superabsorbents are often synthesized from acrylic, acrylonitrile, and acrylamide, all of which are petroleum products. Their effects can harm the environment as they can

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turn into microplastics and pose risks to humans by entering the food chain through contaminated soil and water (Salimi et al., 2020)(Niu et al., 2024). Although natural superabsorbent polymers are more environmentally friendly, they generally have lower water absorption capacities than synthetic options. As a result, efforts have been directed towards improving the water absorption abilities of natural superabsorbent polymers through modification techniques. These methods frequently entail graft copolymerization of polymers containing ample hydrophilic groups (Yang et al., 2024). Research involving graft copolymerization of polymers rich in hydrophilic groups includes the following: Chitosan-Graft-Poly(acrylic acid) Superabsorbents (Jayanudin et al., 2022), Superbsorbent from Starch-g-poly(acrylic acid-co-acrylamide) (Salimi et al., 2020), Superabsorbent hydrogels via graft polymerization of acrylic acid from chitosan-cellulose hybrid (Essawy et al., 2016), superabsorbent polymers based on chitosan derivative graft acrylic acid-co-acrylamide (Fang et al., 2019), and Chitosan-Graft-Poly (Acrylic Acid) Superabsorbent Hydrogel (Barleany et al., 2016).

The synthesis of chitosan-based superabsorbent grafted with polyacrylic acid typically uses NN'-methylene-bis-acrylamide (MBA) as a crosslinker. The addition of MBA influences the absorption and water retention capacity due to the crosslinking density effect within the polymer chains (Rizwan et al., 2024). The objective of this study is to determine the influence of the weight of NN'-methylene-bis-acrylamide (MBA) as a crosslinker in the synthesis of Chitosan-graft-poly (acrylic acid) superabsorbent on the swelling capacity and water holding in sandy soil for agricultural applications.

MATERIALS AND METHOD

Materials

Acrylic acid p.a., 99% purity, with CAS Number: 79-10-7 was produced from Sigma-Aldrich. Chitosan, with a degree of deacetylation (DD) of 87.2%, was obtained from PT. Biotech Surindo. Potassium hydroxide pellets for analysis emsure, labeled Merck 105033, were used. N,N'-methylenebisacrylamide (MBA), CAS Number: 110-26-9, was sourced from Sigma-Aldrich. Ammonium persulfate (APS), with CAS Number: 7727-54-0, was acquired from Merck. Potassium sodium tartrate tetrahydrate was obtained from MERCK.

Synthesis of Superabsorbent From Chitosan-Graft-Poly (Acrylic Acid)

The process of synthesizing the superabsorbent began with the dissolution of 7.88 g of potassium hydroxide in 100 mL of distilled water, which was then utilized to neutralize 15 mL of acrylic acid, followed by stirring for 15 minutes. The neutralized acrylic acid was then left to stand for 24 hours. The subsequent step involved preparing a chitosan solution with a concentration of 4% (w/v) using a 2% (v/v) acetic acid solvent. To this chitosan solution, the initiator, ammonium persulfate (0.05 g in 5 mL of distilled water), was added, and then the mixture was combined with the neutralized acrylic acid solution. The resulting solution was stirred at a speed of 500 rpm at a temperature of 70°C. After 5 minutes, N,N'-methylene bis-acrylamide (MBA) in amounts of 0.015 g, 0.05 g, and 0.1 g were successively added, and stirring continued until a superabsorbent gel was formed. The Chitosan-graft-poly (acrylic acid) superabsorbent was subsequently dried at 65°C for 24 hours or until its weight remained constant.

Determination of Swelling

0.5 g of dry superabsorbent was placed inside a tea bag and immersed in 200 mL of tap water at ambient temperature. The water absorption of the superabsorbent was assessed at defined time points of 1, 3, 5, 12, and 24 hours. Subsequent to sample collection, the water absorption capacity was determined utilizing Eq. (1).

$$Swelling\ (g/g) = \frac{m_1 - m_0}{m_0} \qquad (1)$$

Where m_1 and m_0 were swollen and dry weight of sample.

Water Holding and Water Retention of Sandy Soils

Water holding capacity and water retention in sandy soil were modified from the research reported by Motamedi et al (2020). Superabsorbent was mixed with dry sandy soil at a composition of 1 g SAP per 100 g of sandy soil and placed in a transparent container. Water was slowly added to the container to observe seepage from the bottom. The container was weighed before adding water (W_i) and when water seepage stopped from the bottom of the container, then weighed as (W_f). The soil's water holding capacity (WHC %) was determined using Eq. (2).

$$WHC\ \% = \frac{W_f - W_i}{W_f}\ x\ 100 \qquad (2)$$

The water retention of sandy soil was determined using the procedure refers to the research reported by Wang et al (2014). 100 g of sandy soil was mixed with 1 g of superabsorbent and then placed in a tube with its bottom lined with nylon and weighed (W_0). The sandy soil sample containing the superabsorbent was slowly added tap water from the top, after no water seeped out of the tube, it was then weighed again (W_1). The tube was kept at room temperature, and the weight was measured every day (W_t) until the eighth day. The water retention of sandy soil was calculated using equation 3.

$$WR\ (\%) = \frac{W_t - W_0}{W_1 - W_0}\ x\ 100 \qquad (3)$$

Reusability

The reusability of SAP samples was conducted according to the procedure outlined by Fang et al (2019), which involved the following steps: 0.5 g of pre-crushed sample was placed into a tea bag and submerged in 200 mL of deionized water for 24 hours. The water absorption of the superabsorbent polymer sample was determined using equation (1). Subsequently, the swollen samples were dried in an oven at 65°C until reaching a constant weight. The process of soaking and drying the superabsorbent was repeated approximately 4 to 5 times, and the water absorption capacity was calculated for each swelling condition.

Morphological Analysis of Superabsorbent

Superabsorbent morphology analysis was carried out using a SEM instrument (Evo 10-Carl Zeiss) coated with Au using a voltage of 10 kV.

RESULTS AND DISCUSSION

Influence of Cross-Linker Quantity on Swelling Ratio of Superabsorbent

Chitosan-g-poly (acrylic acid) based superabsorbent were prepared with varying weights of the crosslinker N,N'-methylene bisacrylamide (MBA). MBA plays a crucial role in forming the three-dimensional network structure of SAPs, which directly impacts their ability to absorb and retain water. The concentration of MBA used during synthesis strongly affects the density of crosslinking within the polymer matrix. Figure 1 shows the effect of MBA weight on the swelling of the superabsorbent.

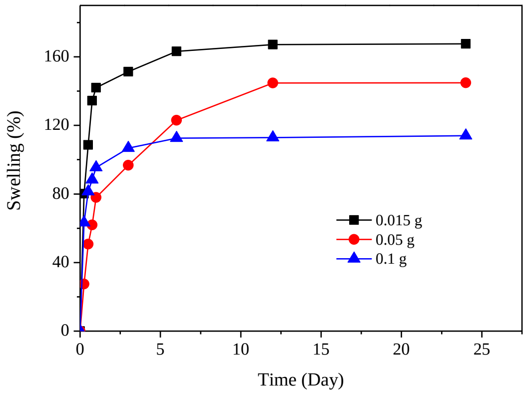

Figure 1. Effect of N,N'-methylene bisacrylamide (MBA) weight on the swelling of the superabsorbent.

Figure 1 shows that the weight of the crosslinker affects the swelling ratio of the superabsorbent. As the weight of MBA decreases, the swelling ratio increases. The highest swelling ratio is produced by the superabsorbent prepared with a crosslinker weight of 0.015 g, reaching a maximum swelling ratio of 167.55 g/g from 15 minutes to 24 hours. In contrast, the superabsorbent prepared with 0.1 g of MBA does not show a significant increase in the swelling ratio and results in the lowest value of 113.98 g/g. The concentration of MBA increases in the synthesis of superabsorbent led to a denser network structure, resulting in reduced swelling capacity due to restricted water molecule penetration. Conversely, lower concentrations of MBA resulted in a looser network structure, allowing for higher swelling capacity but potentially lower water retention due to a less structured matrix (Ibrahim et al., 2019). The same results were also reported by Chavda and Patel (2011) and Pourjavadi and Mahdavinia (2006) that increasing the concentration of MBA can decrease the swelling ratio.

Reusability of Superabsorbent

The reusability of superabsorbent serves to reduce environmental pollution and also has high economic value. The reusability of the superabsorbent is shown in Figure 2.

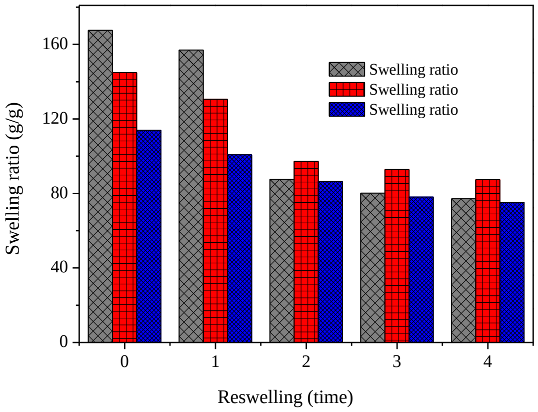

Figure 2. Reusability of superabsorbent based on differences in MBA weight.

Figure 2 shows that the swelling ratio decreases as the swelling-drying cycles increase. Reswelling tests were conducted four times or four cycles, and it can be seen that there is a nearly twofold decrease in the ability to absorb water. In the first cycle, the swelling ratio is still high, namely 157.04 g/g, 130.58 g/g, and 100.8 g/g for superabsorbent prepared with 0.015 g, 0.05 g, and 0.1 g of MBA, but it decreases drastically in the fourth cycle to 87.42g/g, 77.12 g/g, and 75.24 g/g for superabsorbent with a crosslinker weight of 0.015 g, 0.05 g, and 0.1 g. This is due to the fact that the polymer structure gradually deteriorates (Zhang et al., 2019). Despite the decrease in water absorption capacity, these superabsorbent can still be reused, thus saving costs due to their long service life.

Water Holding

The analysis of water holding capacity in sandy soil aims to determine the ability of the sandy soil to retain water for a certain period. In agriculture, the quantity and quality of crop production depend on the efficiency of water use, water application strategies, and soil water holding capacity. Sandy soil has poor physical soil properties and is unable to retain sufficient water (Banedjschafie and Durner, 2015). The function of sandy soil in retaining water can be improved by adding superabsorbent. Figure 3 shows the water holding capacity of sandy soil when supplemented with superabsorbent.

Figure 3 illustrates the differences in water holding capacity in sandy soil mixed with superabsorbent made based on changes in crosslinker weight. The three types of superabsorbent show no significant differences, namely 56.52%, 57.26%, and 56.89% for superabsorbent made with crosslinker weights of 0.015 g, 0.05 g, and 0.1 g, respectively. In contrast, pure sandy soil has a low water holding capacity of only 28.57%, demonstrating that sandy soil has a low ability to retain water. Research conducted by Jayanudin et al (2022) found the water holding capacity of sandy soil to be around 67.4%.

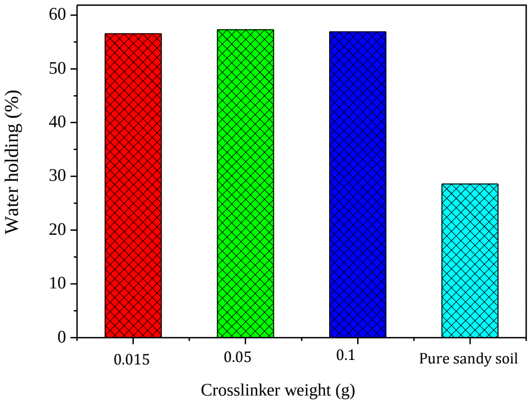

Figure 3. The effect of MBA crosslinker weight on the water holding capacity of superabsorbent in sandy soil.

Water Retention

The influence of adding superabsorbent synthesized based on different crosslinker weights can be seen in Figure 4.

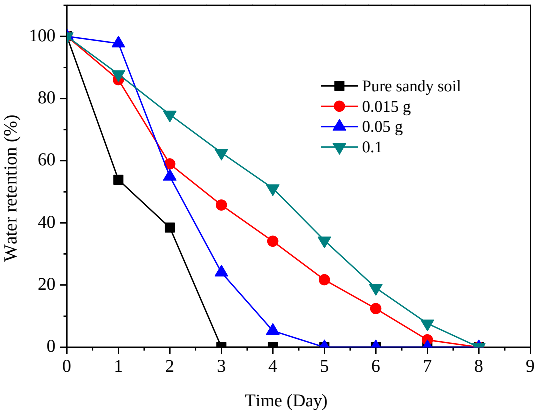

Figure 4. The effect of adding superabsorbent made with varying MBA crosslinker weights on water retention in sandy soil.

Soil water retention (SWR) measures the amount of water that a specific type of soil can hold.

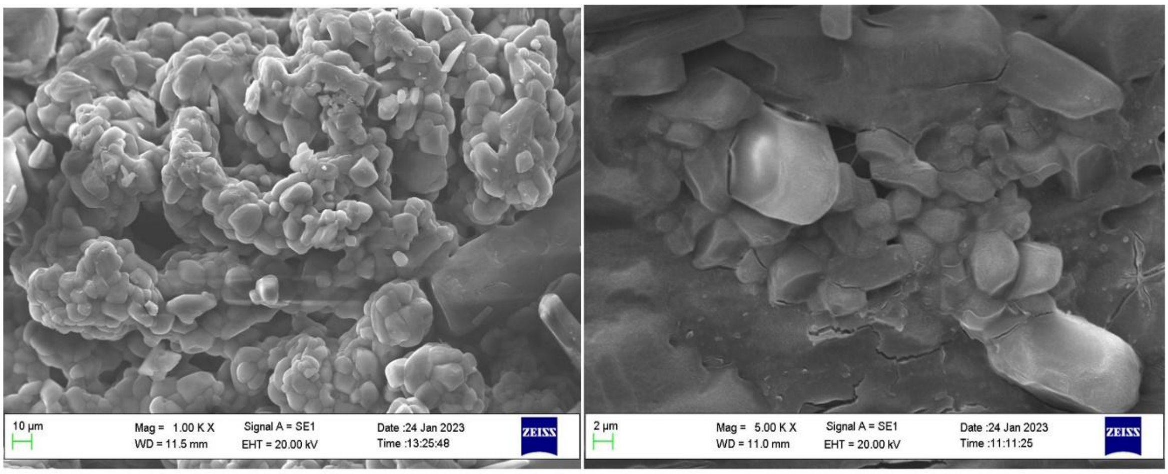

Figure 5. Morphological analysis of chitosan-g-poly (acrylic acid) superabsorbent.

This is a crucial soil characteristic linked to the distribution of pore space, and it is significantly influenced by the soil's structure and texture, as well as other related properties such as soil organic matter (Panagea et al., 2021). Figure 3 shows that pure sandy soil can retain water for about 3 days, whereas sandy soil supplemented with superabsorbent can retain water for up to 4-8 days. Especially for sandy soil supplemented with superabsorbent with a crosslinker weight of 0.1 g, which still contains 9.33% of water. Increasing the crosslinking concentration leads to a higher crosslinking density, which reduces the space between copolymer chains. (Pourjavadi et al., 2005). Consequently, the resulting highly crosslinked and rigid structure cannot expand to hold a large quantity of water.

Analysis of Superabsorbent Morphology using Scanning Electron Microscope (SEM)

The morphology analysis of superabsorbent made based on different MBA crosslinker weights can be seen in Figure 5.

Figure 5 shows that the morphology of chitosan-g-poly (acrylic acid) superabsorbent exhibits clusters on the surface and also visible pores. Connected pore structures are observed, which function to increase water absorption capacity and absorption rate. The superabsorbent appears dense, thus affecting its absorption capacity and water retention ability. The density of superabsorbent is influenced by the addition of MBA due to the crosslinking effect that occurs within its polymer chains (Rizwan et al., 2024).

The results of this study indicate that the addition of superabsorbent can affect water retention. Water retention in soil refers to the soil's ability to store water, which can then be utilized by plants. The importance of water retention in soil for agricultural land cannot be underestimated as it is directly related to plant productivity and health. Figures 3 and 4 show an increase in water holding and water retention with the addition of superabsorbent.

CONCLUSION

The synthesis of chitosan-based superabsorbent grafted with acrylic acid and crosslinked with N,N'-methylene-bis-acrylamide (MBA) has been successfully conducted. The change in MBA crosslinker weight affects the density of the superabsorbent. An increase in MBA weight leads to increased superabsorbent density, thus reducing its water absorption capacity. However, it reduces water loss due to evaporation, as indicated by the increase in its water retention analysis. The research results show the highest swelling ratio of 167.55 g/g, a water holding capacity of 57.26%, and sandy soil mixed with superabsorbent crosslinked with 0.1 g MBA capable of retaining water for up to 8 days at 9.33%

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